AN ANALYTICAL TECHNIQUE FOR SCREENING PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER

by James A. Kammer and Jacob Gibs

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CONVERSION FACTORS

For the use of readers who prefer to use inch-pound units rather than the metric (International System) units used in this report, the following conversion factors may be used (abbreviations are in parentheses):

Multiply metric unit	<u>By</u>	To obtain inch-pound unit
microgram per liter (μg/L)	1	part per billion (ppb)
milligram per liter (mg/L)	1	part per million (ppm)
milligram (mg)	0.00003527	ounce (oz)
gram (gm)	0.03527	ounce (oz)
kilogram (kg)	2.2046	pound (1b)
microliter (μL)	0.0000338	fluid ounce (fl oz)
milliliter (mL)	0.0338	fluid ounce (fl oz)
micrometer (μm)	0.00003937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
degree Celsius (°C)	$F = 1.8 \times {}^{\circ}C + 32$	degree Fahrenheit (°F)

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ABSTRACT

A method for the qualitative and semiquantitative analysis of purgeable volatile organic compounds is described. The method is a modification of U.S. Environmental Protection Agency Methods 601 and 602 for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. Environmental Protection Agency, 1984, Methods for organic chemical analysis of municipal and industrial wastewater, Methods 601 and 602: Appendix A to part 136, volume 49, number 2, Federal Register, 210 pages). The modifications are as follows: a wide-bore capillary chromatography column replaces the packed chromatographic column; the photo-ionization detector and an electrolytic conductivity detector are connected in series; a confirmation chromatographic column is not used; and subambient cooling of the chromatographic column is used. This method analyzes cis-1,2-dichloroethylene and the same 30 priority pollutants specified in Methods 601 and 602. The capillary chromatography column eliminates the coelution of peaks because of increased separation efficiency compared to the packed column used in Methods 601 and 602. Precision of the method is defined for the 30 purgeable priority pollutants and cis-1,2-dichloroethylene. semiquantitative analysis can reduce costs if it is used to characterize samples prior to quantitative analysis by gas chromatography/mass spectrometry. The cost savings result from identifying those samples that do not require quantitative analysis and samples whose high concentrations may cause instrument malfunction on a gas chromatograph/mass spectrometer.

INTRODUCTION

Background

The U.S. Geological Survey's National Water Quality Laboratory (NWQL) in Denver, Colorado, currently analyzes for volatile organic compounds (VOCs) (Wershaw and others, 1987) by a method that is equivalent to U.S. Environmental Protection Agency (USEPA) Method 624 (U.S. Environmental Protection Agency, 1984). USEPA Method 624 is based on purging from water and concentration on an adsorbent of various analytes followed by thermal desorption onto a packed gas chromatographic column. A low-resolution mass spectrometer serves as the measuring device or detector. This is an expensive analysis because of the costs associated with owning and operating a gas chromatograph/mass spectrometer (GC/MS).

One objective of many water-quality investigations is to define the regional extent of manmade pollution in the environment; however, the cost of running organic-chemical analyses on a GC/MS can be a serious constraint in achieving this objective. In general, GC/MS analyses of VOCs done for regional nonpoint-source studies result in only a small percentage (15 to 25 percent) of "hits"--reported sample analyses with concentrations of VOCs greater than the U.S. Geological Survey's NWQL lower reporting limits (T. E. Imbrigiotta, U.S. Geological Survey, written commun., 1987). Because of the

expense of GC/MS analysis and the small percentage of hits, the number of samples that can be analyzed cost-effectively using this method is minimal. Therefore, a more cost-effective VOC analysis method for conducting regional nonpoint-source studies is needed.

The method described in this report is a modification of USEPA Methods 601 and 602 for the quantitative determination of purgeable halocarbons and aromatics (U.S. Environmental Protection Agency, 1984) that can be used as a screening tool for determining the presence or absence of VOCs and their approximate concentrations. The method does not replace GC/MS analysis, but it does determine when GC/MS quantitative measurement is necessary, and whether sample dilutions are indicated. USEPA Method 601 is based on purging from water and concentration on an adsorbent of various halocarbon compounds followed by thermal desorption onto a packed gas chromatographic column. A Hall¹ electrolytic conductivity detector configured to measure halogens functions as the measuring device. USEPA Method 602 differs from Method 601 in the following ways: target compounds are aromatic compounds, a different packed chromatographic column is used, and the measuring device is a photo-ionization detector.

A three-step approach to determine concentrations of VOCs in ground water has been developed for field studies in New Jersey.

- 1. A large number of samples are analyzed semiquantitatively using a gas chromatograph and selective detectors.
- 2. Those samples that have concentrations of VOCs greater than the lower reporting limits of the GC/MS analysis of the U.S. Geological Survey's NWQL or contract laboratories are identified.
- 3. The identified samples are reanalyzed at the U.S. Geological Survey's NWQL or contract laboratories using the quantitative purge-and-trap GC/MS method (USEPA Method 624 or equivalent).

This three-step approach has minimized the cost of analyzing for VOCs, because a less expensive analysis (non-GC/MS) is used to screen the maximum number of samples. This approach also reduces GC/MS instrument downtime caused by analyzing samples with unexpectedly high concentrations of VOCs. Samples that receive GC/MS analysis after step 2 have been characterized by both constituent and concentration so that high concentration samples may be diluted to safe GC/MS operation levels. In addition, the GC/MS sample load is reduced, permitting better use of instrument time.

Purpose and Scope

This report describes a method to analyze surface and ground water for VOCs using a non-GC/MS analysis for a three-step analytical scheme. This method is used to screen water samples for the VOCs listed in table 1. The results of the procedure are qualitative or semiquantitative. The report includes a discussion of sample collection and preservation techniques used, apparatus and reagents used, procedures followed, and safety measures taken.

Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. -- Purgeable volatile organic compound elution order1

Compound	HECD ² retention time (in minutes)	PID ³ retention time (in minutes)
1. Chloromethane		ND ⁴
2. Vinyl chloride		3.90
3. Bromomethane		ND
4. Chloroethane		ND
5. 1,1 Dichloroethylene		7.90
6. Methylene chloride		ND
7. trans-1,2-Dichloroethylene		10.90
8. 1,1 Dichloroethane		ND
9. cis-1,2-Dichloroethylene		14.30
0. Chloroform		ND
1. 1,1,1 Trichloroethane		ND
2. Carbon tetrachloride		ND
3. Benzene		17.00
4. 1,2-Dichloroethane		ND
5. Trichloroethylene		18.80
6. 1,2-Dichloropropane		ND
7. Bromodichloromethane		ND
8. 2-Chloroethyl vinyl ether		21.25
9. trans-1,3-Dichloropropene		21.75
0. Toluene		22.50
1. cis-1,3-Dichlopropene		23.35
2. 1,1,2 Trichloroethane		ND
3. Tetrachloroethylene		23.30
4. Dibromochloromethane	25.10	ND
5. 1-Chloro-3-fluorobenzene		
(internal standard)		25.75
6. Chlorobenzene		26.85
7. Ethylbenzene	ND	27.00
28. 1-Chloro-2-fluorobenzene (field		07.65
surrogate		27.65
9. Bromoform		ND
0. 1,1,2,2 Tetrachloroethane		ND
1. 1,3 Dichlorobenzene		33.90
2. 1,4 Dichlorobenzene		34.20
33. 1,2 Dichlorobenzene	35.30	35.25

¹ Column conditions: 2.0-micrometer-Thick bonded stationary phase on 0.75-millimeter outside diameter x 60 meter-long capillary column with helium carrier gas at 5 milliliter per minute flow rate. Column temperature held at 10 °C for 7.5 minutes, then programmed at 4.5 °C per minute, to 140 °C and held for 0.2 minutes, then programmed at 15 °C per minute to 160 °C and held for 2.1 minutes.

² Hall electrolytic conductivity detector

³ Photo-ionization detector

⁴ Not detected

Summary of Method

Helium is bubbled through a known volume of sample water to remove VOCs in solution. The purged halocarbons and aromatics are adsorbed on a selective trap. After purging is completed, the trap is rapidly heated and backflushed with helium to desorb the compounds onto the chromatography column. The column is then heated at a programmed rate so that each compound has a unique retention time. The eluted compounds are detected with a pair of selective detectors connected in series. Peaks representing a compound or group of compounds are integrated using microcomputers to determine approximate concentrations.

This method differs from USEPA Methods 601 and 602 (U.S. Environmental Protection Agency, 1984) in that (1) it uses a wide-bore capillary column instead of a packed chromatographic column (Supelco, Inc., 1984), (2) it eliminates the confirmation chromatographic column, (3) it connects the photo-ionization detector (PID) and Hall electrolytic conductivity detector (HECD) in series, and (4) column temperatures below ambient temperature are used to improve resolution and compound separation of the VOCs that are gases at room temperature. This method eliminates peak coelution and reduces peak tailing.

The compounds detected are shown in table 1. All compounds except benzene, toluene, and ethyl benzene are detected on the HECD detector. Table 1 shows that 14 of the 31 compounds are detected by both the HECD and PID detectors.

SAMPLE COLLECTION AND PRESERVATION

Borosilicate glass vials of 25-mL (milliliter) capacity or larger are used to collect water samples for analysis. They are equipped with a hole in the center to accommodate a Teflon-lined silicon septum. Both vials and septa are washed with detergent and rinsed with tap and distilled water. Vials and septa are baked for 1 hour at 400 °C (degrees Celsius) and 105 °C, respectively, before use. The vials are filled, with a minimum of aeration and agitation, to overflowing. The cap and septum are used to seal the vial so that no air bubbles are trapped inside. Samples are preserved by chilling on ice or refrigeration at 4 °C until the time of analysis. Caps are retightened after the sample is chilled to minimize air bubbles in the sample. It is desirable to run samples within 14 days of collection for optimal results.

APPARATUS

Purge-and-Trap Sample Concentrator

The purge-and-trap sample-concentrator system needed for this method consists of a purging device, adsorbent trap, and a desorption system (Tekmar Company Model LSC-2 or equivalent). The purging device is designed to accept 5- and 25-mL glass sparging vessels and maintains a water column at least 3 cm (centimeters) deep. The gaseous headspace between the water column and the trap has a total volume of less than 15 mL. The purge gas is introduced at a point no more than 5 mm (millimeters) from the base of the water column. The purge gas passes through the water column as finely

divided bubbles with diameters of less than 3 mm at their origin. The trap unit contains 100 mg (milligrams) of Tenax TA Grade (60/80 mesh) adsorbent resin and 75 mg of activated coconut charcoal. The trap has an internal diameter (ID) of 0.27 cm and is at least 25 cm long. The desorption system must be capable of rapidly heating the trap from collection temperature (~30 °C) to desorption temperature (180 °C).

Gas Chromatograph

The gas chromatograph is an analytical system that includes the following features: temperature programming; subambient cooling; a widebore capillary chromatography column; carrier, make-up, and reactor gases; an HECD and a PID; and two integrators (microcomputers) for determining areas under the peaks.

Column

The column (Supelco, Inc., Vol-Col or equivalent) used is a 60-m (meter)-long glass capillary tube with a bonded stationary phase. The internal dimensions are 0.75 mm ID with a $2.0-\mu m$ (micrometers)-thick bonded stationary phase.

Detectors

The two detectors used in this method are a photo-ionization detector to detect unsaturated compounds, and a Hall electrolytic conductivity detector (Tracor Instruments Austin, Inc. HECD Model 700-A) to detect halogenated compounds. The combination of the two detectors in series can identify all 30 volatile organic priority pollutants (13 of which can be identified by both detectors) and cis-1,2-dichloroethylene.

Syringes

Suitable syringes include gas-tight glass 5-mL and 25-mL syringes with Teflon luer-loc tips and shut-off valves, and an assortment of microsyringes of 5-, 10-, 25-, and $100-\mu L$ (microliters) capacity.

REAGENTS

Reagent-Grade Water

Reagent-grade water is defined as a water that does not contain detectable levels of any compounds listed in table 1. It is used to rinse syringes, to dilute samples, and to prepare blanks and standards.

Reagent-grade water may be purchased from a commercial supplier. It also may be prepared by a variety of methods: passing tap water through a carbon-filter bed containing approximately 0.5 kilograms of activated carbon; using a commercial water-purification system; or boiling tap water for 15 minutes and sparging with a contaminant-free inert gas for 1 hour while maintaining a water temperature of at least 90 °C. Reagent-grade water always must be tightly sealed when not being used to prevent its contamination.

Standards

Standard stock solutions for compounds of interest are available either singly or in mixtures as USEPA-certified solutions. Various concentrations of standards can be prepared by diluting stock solutions with methanol. All standard solutions are to be stored at -18 °C in microreaction vessels equipped with gas-tight Teflon shut-off valves. Mixtures are replaced every 4 weeks, or more often if necessary.

The internal standard used is 1-chloro-3-fluorobenzene. 1-chloro-3-fluorobenzene can be used to measure changes in detector response over time because it is detected by both the HECD and PID detectors, and because it is rarely found in the environment. The retention time is found in table 1.

A surrogate compound, 1-chloro-2-fluorobenzene, may be added to the sample in the field. Because this compound is rarely found in the environment, it can be used to judge sample integrity. The retention time is found in table 1.

Methanol

Reagent or chromatographic-grade methanol is used for purge-and-trap applications. It has been analyzed and certified to be exceptionally free of interferences for the analysis of purgeable priority pollutants. It is used to clean glassware and to prepare standard dilutions.

Phosphoric Acid

A 20-percent solution of reagent-grade phosphoric acid and distilled water is used for cleaning glassware.

n-Propanol

The electrolyte for the HECD is a solution of 75-percent reagent-grade n-propanol (distilled-in-glass, high-purity solvent) and 25-percent reagent-grade water by volume instead of the 100-percent n-propanol specified by USEPA Method 601. This change increases the sensitivity of the detector for chlorinated and brominated compounds and enables the detection of some fluorinated compounds. Table 2 shows that the average relative improvement in detector response relative to that obtained with 100-percent n-propanol for 15 compounds is 218 percent. An additional benefit is reduced peak width and decreased peak asymmetry that results in improved peak resolution. Both changes in the detector response are caused by the rapid dissolution of the acid vapors into the new electrolyte, which is more polar than the standard 100-percent n-propanol electrolyte. These effects are largest for organic compounds containing fluorine or bromine, which form weak acids in the HECD.

The electrolyte mixture used in this report has approximately the same volumetric proportions as the azeotrope of water and n-propanol (76 percent and 24 percent, respectively) (Weast and others, 1988). Therefore, the electrolyte composition should not change with time because of differences in evaporation rate. A changing electrolyte composition would cause changes in the detector response.

Table 2.--Effect of changing the electrolyte solution from 100-percent n-propanol to 75-percent n-propanol. 25-percent water, by volume, on the response of the Hall electrolytic conductivity detector

Compound	Change in detector response ¹ (percent) ²	Change in peak width at half-height ¹ (percent) ²
trans-1,2-Dichloroethylene	73.0	-24.1
cis-1,2-Dichloroethylene	109.	-27.4
1,1,1-Trichloroethane	206.	-32.9
1,2-Dichloroethane	59.3	-38.1
Dichlorobromomethane	226.	-25.0
trans-1,3-Dichloropropene	197.	-34.9
cis-1,3-Dichloropropene	115.	-49.5
Chlorobenzene	306.	-23.8
1-chloro-2-fluorobenzene (field surrogate)	305.	-15.6
1-chloro-3-fluorobenzene (internal standard)	319 .	-24.5
Bromoform	325.	-7.2
1,1,2,2-Tetrachloroethane	240.	-26.6
1,3-Dichlorobenzene	380.	-2.3
1,4-Dichlorobenzene	241.	-28.1
1,2-Dichlorobenzene	172.	-38.3
Mean	218.	26.6

Based on three replicate analyses at 8 micrograms per liter for each compound

² Change in detector response or peak width at half-height,

Gases

Three gases are required in this method. Prepurified hydrogen (99.99-percent pure) is used in the HECD thermal reactor to create a hydrogen-rich reducing atmosphere. High-purity helium (99.997-percent pure) is used as the purge gas to remove analytes from the aqueous sample, as the chromatographic carrier gas, and as the make-up gas for the two detectors. Compressed air operates the autosampler (Tekmar Co. Model ALS), which analyzes several samples sequentially unattended.

PROCEDURE

The operating conditions used for the gas chromatograph are summarized in table 3. If chromatographic conditions or equipment are varied from those shown in table 3, compound separation and retention times may vary from those reported in table 1. An example of compound separation using these operating conditions is shown in figure 1.

Dilute standards are prepared from the stock standards for all compounds of interest prior to sample analysis. It is desirable to run at least four concentrations for each compound. Expected sample-response levels are bracketed between the highest and lowest concentrations in the standard curve. The difference between concentrations on the standard curve ideally should be less than a factor of five. A linear response is desirable for the concentration range of interest for all compounds in the standard solutions. If a linear response is not achieved for any compound, additional standards need to be run to determine the source of error.

Once the standard curve has been established, a blank and a standard of known concentration are run. These analyses should be within the acceptable limits for cleanliness and linearity, respectively, before analysis of samples begins. The following procedure is followed:

Adjust the flow rate of the purge gas (helium) to 40 mL/min (milliliters per minute). Bring the sample to ambient temperature (approximately 25 °C), then pour the blank water or sample into a 5-mL gas-tight syringe equipped with a Teflon shut-off valve. Insert the plunger, being careful to remove any air that might become entrapped within the syringe. Adjust the plunger to deliver exactly 5 mL, and add standards and/or the internal standard with a microliter syringe to the 5-mL syringe. Because future analyses from the opened sample bottle are invalid, fill a second syringe (also equipped with a Teflon shut-off valve) immediately and refrigerate the second syringe promptly. The refrigerated second syringe of sample is analyzed at ambient temperature.

Attach the syringe valve on the syringe to the syringe port of the sparging vessel. Open the valve and port, and inject the blank or standard or sample into the vessel. Close the port and purge for $11 \ (+/- 0.1)$ minutes at ambient temperature (<30 °C). After the purging cycle is completed, rapidly heat the trap to 175 °C and begin desorbing the sample onto the cooled (10 °C) column. When the temperature of the trap reaches 180 °C, start the temperature program of the GC.

Table 3.--Chromatographic conditions

[--, not applicable; °C, degrees Celsius; <, less than]

FLOW RATES

(in milliliters per minute)

Gas (use)	GC¹	Purge-and-trap	Auto- sampler	HECD ²
Helium (purge)		40	40	
Helium (carrier)	5			
Helium (make-up)	3 5			
Hydrogen				30

GC SETTINGS

Initial temperature Initial hold	
	4.5 °C per minute to 145 °C
Hold	
Final ramp	15 °C per minute to 160 °C
Final hold	2.1 minutes
Time	40.8 minutes
HECD ² detector	250 °C
PID ³ detector	225 °C

PURGE-AND-TRAP SETTINGS

Inlet 110 °C

Trap temperature	<30 °C
Purge time	11.0 minutes
Desorb temperature	180 °C
Desorb time	4.0 minutes
Bake temperature	205 °C
Bake time	21 minutes

DETECTOR SETTINGS

HECD solvent flow	5 milliliters per minute
HECD reactor temperature	850 °C
PID voltage	0.15 Volts

¹ Gas chromatograph

² Hall electrolytic conductivity detector

³ Photo-ionization detector

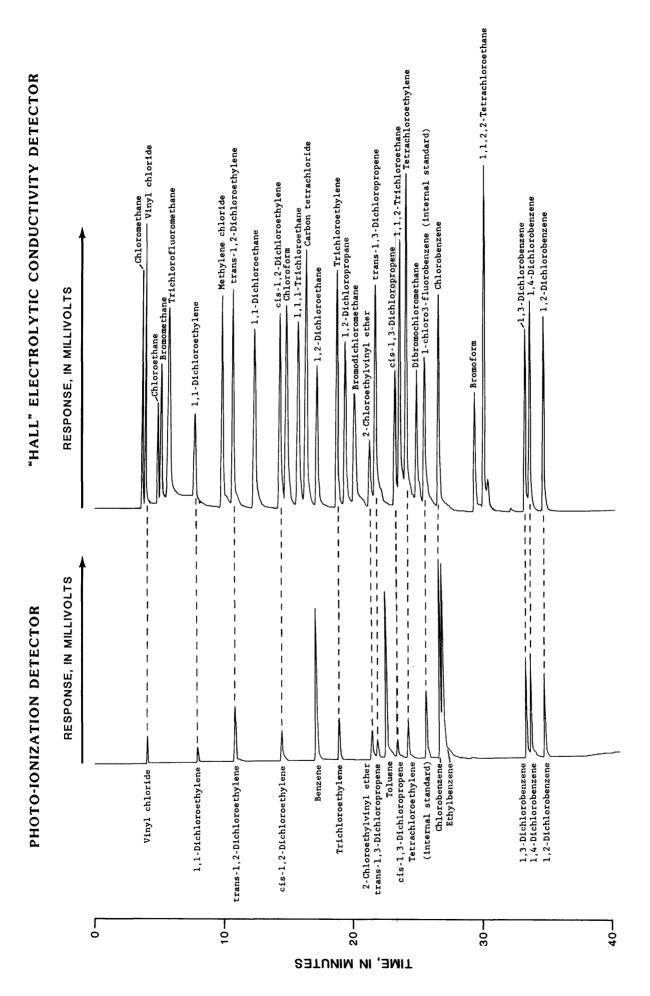


Figure 1.--Chromatograms of 31 compounds measured by the Hall electrolytic conductivity detector and the photo-ionization detector.

After desorbing the sample for 4 minutes at 180 °C, thermally condition the trap at 205 °C for 21 minutes to remove materials not transferred to the gas chromatograph. This will help to minimize cross-contamination. After the trap cools to 30 °C, another sample may be purged.

Inspect the chromatogram and identify the compounds by matching the retention times of the chromatogram with those of the standards and by comparing respective times on the PID and HECD. Compare the peak areas with those on the standard curve to determine the concentration range for each observed compound of interest.

If the peak-area response for any peak is larger than that of the highest concentration used in the standard curve, a sample dilution must be prepared. Dilute the sample from the second (refrigerated) syringe by adding reagent grade water to the purging vessel, a volume of sample such that the sum of the two equals 5 mL. Prior to adding a sample to the purging vessel, the internal standard should be added to the sample syringe.

Calculations

Compound concentrations are classified and reported by the following concentration ranges, in $\mu g/L$ (micrograms per liter): x < 0.8, $0.8 \le x < 3$, $3 \le x < 10$, $10 \le x < 40$, $40 \le x < 100$, and $x \ge 100$, where x is the compound concentration. The detector responses for the 31 target compounds of each concentration range are determined using external standards. Interferences are measured from system and water blanks that are performed on the same day that sample analyses are performed. Corrections for the blank interferences are made by subtracting interference peak areas from the most recent blanks from sample peaks with the same relative retention time.

Quality Control

Reagent-grade water blanks are run at both the beginning and end of the day to verify that the system is free from contamination. If samples contain large amounts of purgeable compounds, blanks are run before additional samples are analyzed to verify cleanliness of the system. Standard mixtures also are run at both the beginning and end of the day to insure that machine response for all compounds remains linear and that operating conditions remain constant. If response deviates significantly, operating conditions (carrier gas flow, leak checking, and so forth) are examined, corrected, and a new standard curve is established before additional samples are run.

Interferences

Contamination of apparatus and reagents by VOCs is the most common interference in this analysis. Non-Teflon products such as plastic tubing or flow controllers with rubber components that could absorb VOCs are not to be used in the purge-and-trap analysis apparatus.

Cross-contamination from a previous sample can be avoided by running blanks after samples with high VOC concentrations. If necessary, the column and trap is conditioned at high temperature (~215 °C) and the hardware is cleaned and baked before additional samples are run. Sample syringes are

rinsed thoroughly with reagent-grade water between samples. Sparging vessels are soaked in a mild phosphoric acid solution, rinsed thoroughly with reagent-grade water followed by reagent-grade methanol, and heated at ~105 °C for 1 hour. Frequent high-temperature conditioning of the entire system is used to eliminate interferences.

Precision

Precision for this method is presented as coefficient of variation in table 4. The coefficient of variation for each compound is based on seven replicates at a concentration of 7 μ g/L.

SAFETY

Many of the reagents used in this method are known carcinogens, and, although the toxicity of others has not been established precisely, they should all be treated as potential health hazards. Exposure to these chemicals should be minimized. The use of solvent-resistant gloves and fume hoods is highly desirable when preparing standards. When high concentrations of these compounds are suspected in samples or prepared in standards, the use of a toxic-gas respirator is strongly encouraged.

REFERENCES

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- Wershaw, R. L., Fishman, M. J., Grabbe, R. R., and Lowe, L. E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the U.S. Geological Survey, book 5, chap. A3, 80 p.

Table 4.- System precision at a concentration of 7 micrograms per liter

Compound	Coefficient of variation, in percent
Chloromethane	9.7
Vinyl chloride	
Bromomethane	
Chloroethane	• • • • • • • • • • • • • • • • • • • •
1,1 Dichloroethylene	
Methylene chloride	• • • • • • • • • • • • • • • • • • • •
trans-1,2-Dichloroethylene	
1,1 Dichloroethane	
cis-1,2-Dichloroethylene	
Chloroform	
1,1,1 Trichloroethane	
Carbon tetrachloride	
Benzene	
1,2 Dichloroethane	
Trichloroethylene	
1,2 Dichloropropane	
Bromodichloromethane	
2-Chloro vinyl ether	
trans-1,3-Dichloropropene	
Toluene	
cis-1,3-Dichloropropene	
1,1,2 Trichloroethane	
Tetrachloroethylene	
Dibromochloromethane	
Chlorobenzene	
Ethylbenzene	7.6
Bromoform	
1,1,2,2 Tetrachloroethane	
1,3 Dichlorobenzene	
1,4 Dichlorobenzene	
1,2 Dichlorobenzene	